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GENESIS OF CLAY MINERALS IN PRE-CAMBRIAN METAMORPHOSED SEDIMENTARY ROCKS

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Abstract: The presence of high-alumina minerals such as kyanite, sillimanite etc. in Pre-Cambrian schists (or gneisses) is often treated as resulting from the metamorphism of terrigeneous kaolinite in sedimentary rocks. This implies the existence of kaoline weathering crusts. The study of Late Archean to Early Proterozoic residual rocks of the weathering crust indicates, however, that they are of montmorillonite-illite or chlorite-illite composition. The association of high-alumina minerals with carbonic matter (in the case of Early Proterozoic high-alumina concretion schists of the Kola Peninsula, Baltic Shield), as well as the geochemical peculiarities in the distribution of REE and other microelements in the rocks in question, their position in the section, and thermodynamic calculations of kaolinization for various minerals suggest an authigenic, diagenetic origin and subsequent metamorphism for kaolinite and clay concretions.

Key words: clay minerals, residual rocks of the weathering crust, sedimentary rocks, carbonaceous high-alumina concretions, kaolinite, organic matter, diagenesis, Kola Peninsula.

The nature of clay minerals in sedimentary rocks is controlled by two principal factors: 1 - the mineral composition of the rocks of alimenting provinces, and 2 - the conditions of the environment in the sedimentation basins that affect the alteration of the allotigeneous material. Clay minerals were formed during weathering in the course of the whole geological history of the Earth. The study of residual rocks of the weathering crust varying in age from Late Archean to Cainozoic, within the Eastern European Platform and its folded framework, has shown that these rocks differ in composition (Bobrov & Shchipakina 1989). The principal factors in weathering (atmosphere, hydrosphere, the organic matter, as well as climatic and tectonic conditions and substrate) changed evolutionally during the geological history of the Earth (Holland 1973; Shidlowski 1975; Ronov et al. 1990). Hence the intensity in the transformation of the initial substrate and the composition of clay minerals in the weathering crust residual rocks and in sedimentary rocks varied both qualitatively and quantitatively.

In order to study and to reconstruct the metamorphosed Pre-Cambrian sedimentary rocks the following system was analysed: initial composition of continental rocks (degree of weathering) - composition of sedimentary rocks - alterations in the initial sediment (diagenesis, epigenesis, metagenesis).

The study of Late Archean - Early Proterozoic (2.8 - 2.1 billion years) residual rocks of the weathering crust (Baltic Shield, Ukrainian Shield, Voronezh Massif) has shown that these rocks are metamorphosed and have mostly quartz-micaceous or quartz-chloritic composition (Bobrov & Shchipakina 1991). Their metasedimentary equivalents are represented by arkosic metasandstones, gravelites and by conglomerates, quartz-sericitic (biotitic and chloritic) schists or various gneisses having a wide range of combinations of the minerals mentioned.

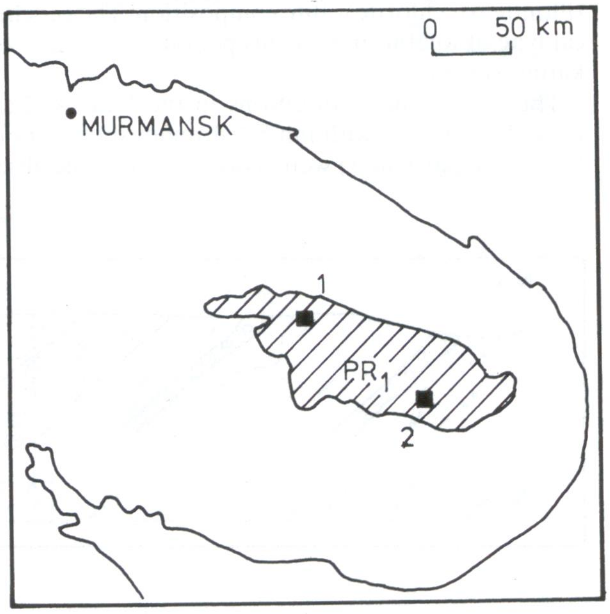

Fig. 1. Scheme of the position of the Early Proterozoic deposits containing high-alumina carbon-bearing concretion schists. The regions studied: 1 - mountain Shuururta, 2 - mountain Nussa.

Table 1: Chemical compositions of the samples studied.

	1	2	3	4	5	6	7	8	9	10
	n=4	n=5	n=3	n=10	n=10	n=10	n=4	n=3	n=3	n=3
SiO_2	74.71	62.46	75.15	35.60	49.76	50.12	47.56	44.62	60.23	59.24
TiO_2	0.53	1.13	0.66	1.40	1.08	1.81	0.66	0.43	1.28	1.63
Al_2O_3	12.70	19.78	13.24	58.23	37.90	41.86	45.86	51.69	32.13	29.53
Fe_2O_3	1.27	4.48	4.01	0.49	0.84	1.23	0.21	0.20	1.28	0.78
FeO	3.77	9.04	2.58	-	0.30	0.40	0.10	0.10	0.98	2.12
MnO	0.05	0.33	0.05	0.01	0.03	0.01	0.01	0.01	0.01	0.02
MgO	0.70	0.82	0.72	0.11	0.16	0.13	0.24	0.20	0.03	0.01
CaO	0.78	0.24	0.36	0.12	0.14	0.15	0.20	0.20	0.14	0.60
Na_2O	1.04	0.03	0.20	0.23	1.02	0.08	0.20	0.28	0.33	1.43
K_2O	2.45	0.02	0.82	0.03	4.38	1.26	0.15	0.36	1.11	2.12
P_2O_5	0.17	0.14	0.12	0.05	0.06	0.08	0.05	0.03	0.08	0.16
L.O.I.	1.31	1.19	1.98	2.96	4.08	3.16	2.02	1.88	2.13	2.70
Total	99.48	99.66	99.92	99.23	99.73	100.31	99.66	99.90	99.73	100.34
C_{org}	0.36	0.20	0.64	3.96	2.08	3.98	2.46	2.01	0.55	0.44

1 - garnet-muscovitic schists; 2 - garnet-staurolitic schists; 3 - garnet-staurolite-muscovitic schists; 4 - 6: large zonal carbonic-kyanitic concretions: 4 - central part, 5 - medium part, 6 - periphery; 7 - small non-zonal concretions; 8 - small paramorphic concretions; 9 - staurolite-kyanitic schists; 10 - plagioclase-staurolite schists.

The regional metamorphism and the composition of the overlying pararocks being isochemical, the reconstruction of the initial clay substance of the metamorphosed residual rocks of the weathering crust indicates that it has a mixed chlorite-montmorillonite, montmorillonite (or chlorite)-illite composition. The geochemical type of weathering for this period is identified as alkaline-sialitic.

The geochemical conditions in the Late Archean - Early Proterozoic with inhibited removal of bases (potassium in particular) were associated with the absence of vegetation on land and low water exchange in weathering profiles. The absence of mineral forms of trivalent iron and high FeO: Fe_2O_3 ratios (1.0 to 7.8) in the residual rocks of the weathering crust and in their redeposited products imply that the clay mineral associations in question were formed under the reduction conditions of an oxygen-free atmosphere.

However, in many regions of the development of Pre-Cambrian schists (or gneisses) high-alumina minerals are present, such as andalusite, sillimanite, kyanite etc.). Graphite is quite often associated with these minerals.

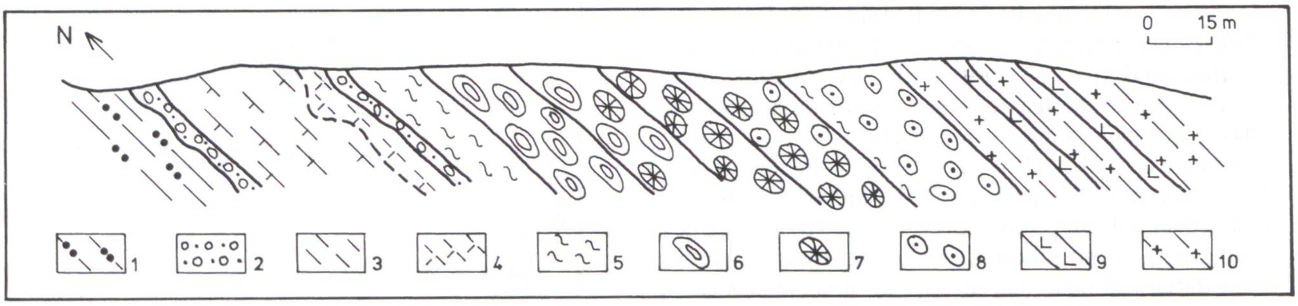

Fig. 2. Scheme of the geologic section of mountain Shuururta region.

Legend: AR_2: 1 - gneisses, 2 - metaconglomerates, metasandstones, 3 - acid metavolcanites, 4 - metamorphosed residual rocks of the weathering crust; PR_1: 5 - garnet-muscovitic, garnet-staurolite-muscovitic and quartz-muscovitic schists, 6 - 8: concretion: 6 - large zonal, 7 - medium sized, 8 - small; 9 - kyanite-plagioclase-staurolitic and plagioclase-staurolitic schists; 10 - orthoamphibolites.

In addition, in kyanite and sillimanite schists (gneisses) of foreign deposits concretion-like formations occur that are described as nodules, residual boulders etc. (Roy 1960). According to some researchers, the presence of high-alumina minerals unambiguously implies the existence of initial allotigeneous kaolinite and, therefore, of kaolinite weathering crusts (Belkov 1963; Golovyonok 1977). On the other hand, high-alumina formations are treated as resulting from acid leaching of the initially heterogeneous substrate (Vishnevskaya et al. 1982). The purpose of the present work was to elucidate the nature of the initial material for high-alumina formations of one of the regions of the Eastern European Platform.

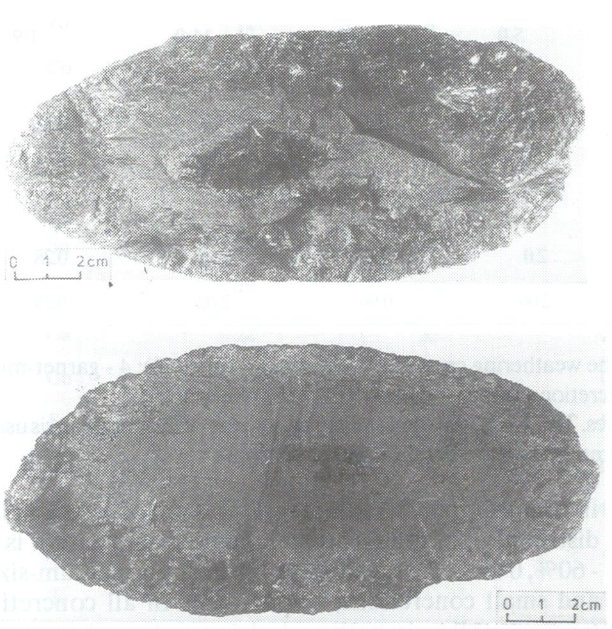

Fig. 3. Samples of zonal carbon-bearing concretions of kyanitic (central part), kyanite-muscovitic (intermediate part) and quartz-muscovite-kyanitic (periphery) composition.

Geological setting

The Early Proterozoic metasandstone-schist layer (Keiv series), which includes carbonaceous, high-alumina (kyanite) concretion formations were studied in the Baltic Shield (Kola Peninsula) (Fig. 1). These formations occur between two horizons of schists (Fig. 2). The lower horizon is represented by garnet-muscovitic, garnet-staurolite-muscovitic and quartz-muscovitic schists, and the upper, by staurolite-kyanitic and plagioclase-staurolitic schists. The underlying schists (on the top) and the overlying schists (in the base foot) contain isolated kyanite crystals and fine-dispersed carbonic matter. The concretions occur in accordance with the stratification of rocks; they are clearly individualized within

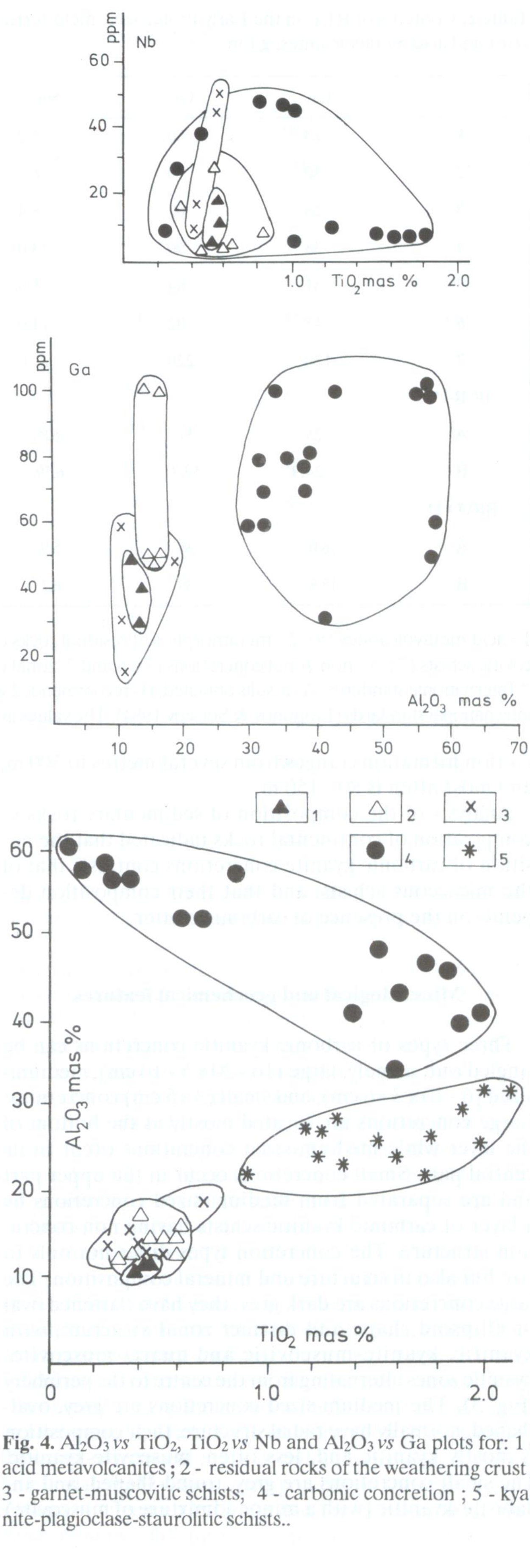

Fig. 4. Al$_2$O$_3$ *vs* TiO$_2$, TiO$_2$ *vs* Nb and Al$_2$O$_3$ *vs* Ga plots for: 1 - acid metavolcanites ; 2 - residual rocks of the weathering crust ; 3 - garnet-muscovitic schists; 4 - carbonic concretion ; 5 - kyanite-plagioclase-staurolitic schists..

Table 2: Contents of REE in the Early Proterozoic meta-terrigenic and underlying Late Archean residual rocks of the weathering crust and acid metavolcanites, g/ton.

	La	Ce	Sm	Eu	Tb	Yb	Lu
1	23	50	5.2	1.2	1.15	4.8	0.83
2	30	70	6.6	1.5	1.5	4.9	0.85
3	26	62	6.4	1.0	1.3	4.5	0.69
4	38	90	13.0	2.4	3.0	11.0	1.7
5	31	64	5.6	1.1	1.1	4.4	0.7
6	43	92	11.0	3.7	4.4	12.0	1.8
7	120	220	21.0	5.0	4.2	11.0	1.9
BCR-1*							
A	25	51	6.8	2.0	1.1	3.4	0.56
B	24.9	53.7	6.59	1.95	1.05	3.38	0.51
BRVO-1*							
A	16.0	38	5.9	2.0	1.0	1.95	0.28
B	15.8	39	6.2	2.06	0.96	2.02	0.29

1 - acid metavolcanites (5); 2 - metamorphosed residual rocks of the weathering crust (5); 3 - metasandstones (3); 4 - garnet-muscovitic schists (7); 5 - non-zonal concretions (7); 6 and 7: zonal concretions: 6 - central part (7), 7 - periphery (7).

* International standards: A - results obtained; B - recommended values. The REE were determined by neutron-activation analysis using international standards (Lyapunov & Sotscov 1984). The values in parentheses represent the number of analyses.

cretion formations ranges from several metres to 300 m, and most often is 80 - 150 m.

Analysis of the composition of sedimentary rocks vs composition of continental rocks indicated that the position of carbonic kyanite concretions contrasts that of the micaceous schists, and that their composition depends on the presence of carbonic matter.

Mineralogical and geochemical features

Three types of carbonic kyanitic concretions can be singled out, namely, large (16 - 20 x 5 - 10 cm), medium-sized (6 - 10 x 3 - 6 cm), and small (3 x 5 cm) concretions. Large concretions are located mostly at the bottom of the layer while medium-sized concretions occur in its central part. Small concretions occur in the upper part and are separated from medium-sized concretions by a layer of carbonic kyanitic schists having non-concretion structure. The concretion types differ not only in size but also in structure and mineral composition. The large concretions are dark grey; they have flattened oval or ellipsoid shape and distinct zonal structure, with kyanitic, kyanite-muscovitic and quartz-muscovite-kyanitic zones alternating from the centre to the periphery (Fig. 3). The medium-sized concretions are grey, oval-shaped, normally have radial structure; their composition is mostly kyanitic and, less often, muscovite-kyanitic. The small concretions are grey, round-shaped, and andalusite-kyanitic (with a minor admixture of muscovite) in composition. Certain regularities are observed in the distribution of muscovite: muscovite composition is 30 - 60%, 0 to 8 - 10%, and up to 1% in large, medium-sized and small concretions, respectively. In all concretion types, as well as in both underlying and overlying rocks carbonic matter is present as graphite or, which is more often, as graphitite. The composition of carbonic matter is 1.5 - 10 % (2.5 - 4 % on average) in the concretion and 0.1 - 0.6 %, less often 1 % and more, in the schists. The carbonic matter is of organic nature, its composition is $C_{org.}$ - 98.70, H - 0.67, CO_3 - 0.33, N - 0.22 (the analyses were performed using a Perkin Elmer CNH analyser). The chemical composition of the rocks under study is given in Tab. 1. The contents of the basic rock-forming components were determined according to the scheme of complete chemical analysis of rocks. The $C_{org.}$ content was determined using the method of Knopp (Ponomarev 1951; Milner 1962).

The highest alumina and the smallest silica contents correspond to the central parts of the concretions. High potassium and sodium contents are characteristic of the medium and outer zones. The Al_2O_3 *vs* TiO_2, TiO_2 *vs* Nb, and Al_2O_3 *vs* Ga plots indicate pronounced anisotropy in the composition fields of carbonic high-alumina concretions with respect to enclosing schists, underlying metasandstones, residual rocks of the weathering crusts and the initial acid metavolcanites (Fig. 4).

A study of the distribution of rare earth elements in the concretion underlying and enclosing rocks has shown that these rocks are similar in composition of

Table 3: Contents of microelements in carbonic-kyanitic concretions and enclosing schists, g/ton.

	1	2	3	4	5	6
Ba	40	28	330	22	140	190
Sr	44	46	150	17	190	85
Rb	193	23	410	11	47	87
Cs	1.9	-	5.6	0.92	1.9	5.5
Cr	37	30	67	24	58	190
V	10	22	12	180	400	600
Ni	12	8	4	19	7	15
Co	0.69	2	2.7	3.7	12	16
Cu	11	40	25	50	52	72
Zn	71	83	220	17	15	73
Pb	25	28	120	5	82	157
Sn	20	7.4	15	7	5.5	22
Mo	0.5	0.64	0.74	2	9.5	4.5
Ga	22	35	28	45	65	93
Ge	-	-	0.2	8	7	0.5
Sc	2.1	2.6	5.1	3.9	64	45
Y	52	91	130	26	13	90
Zr	458	204	400	65	290	440
Nb	50	72	49	54	10	82
Ta	1.6	-	4.1	2.7	0.2	1.2

1 - garnet-muscovitic schists (15); 2 - garnet-staurolite-muscovitic schists (15); 3 - quartz-muscovitic schists (15); 4 - non-zonal concretions (10); 5 - 6 zonal concretions: 5 - central part (10), 6 - periphery (10). The numbers of analyses are given in parentheses.

rare-earth elements but differ in their contents (Tab. 2). In the underlying metavolcanites and residual rocks of the weathering crust light rare-earth elements prevail and a deficit of Eu is observed. Preservation and a small accumulation of rare-earth elements in the residual rocks of the weathering crust is determined by the alkaline character of the weathering process in Late Archean - Early Proterozoic and by sorption of rare-earth elements by clay minerals (illites, montmorillonites, and mixed-layer minerals). A minor fractioning of rare-earth elements is possible during weathering. This process is controlled by variations of pH of the infiltrating waters and is normally limited to the weathering profile. The fractioning in question is also controlled by partly weathered feldspars and newly formed clay minerals (Nesbitt 1979). The transportation of rare-earth elements to the sedimentary cycle is mostly mechanical (Haskin et al. 1966; Ronov et al. 1967; Nesbitt & Young 1982; Taylor & McLennan 1981). The above trend in the distribution of rare earth minerals is also observed in metasandstones, metapellites and non-zonal high-alumina concretions, which implies the existence of a local source of sediments.

The aluminosilicate and silicate matter, weakly differentiated during weathering (feldspars, quartz, mica and illite, chlorite and montmorillonite) that was brought to sedimentation basins was mostly in equilibrium with sea water and was used for formation of sandstones and sandstone clays. The development of organic life in the basins, the accumulation and dying of organic matter in the bottom part leading to high production of carbon dioxide, resulted in an increase of the pH of silt waters and therefore in intensive authigenic mineral (i.e. kaolinite) formation and concretion formation.

The thermodynamic parameters of individual minerals, neutral molecules and free ions in water solution (Garrels & Christ 1965; Naumov et al. 1971; Helgeson 1969) were used in thermodynamic calculations of kaolinization. The calculations show that kaolinization of albite, anortite, micas and chlorite in water solution containing free hydrogen ions is exothermic and spontaneous, with different energy fields for each mineral, whereas the tranformation of microcline, illites and montmorillonites is endothermic. According to the calculated pH values corresponding to the equilibrium between authigenous kaolinite and the initial mineral, the above minerals fall into two groups differing in acid -

base formation conditions: 1 - micas and chlorite, with pH 5.4 - 6.9, and 2 - feldspars, illites, and montmorillonites, with pH 7.6 - 9.3.

The pH values for the sea water range from 7.5 to 8.5 (Vinogradov 1967; Garrels & Mackensie 1971); for silt waters pH is 7.5 - 8.0 and for bottom waters, pH is 8.1 - 8.5. Under these conditions, authigeneous kaolinite is not formed because most of the minerals in question are stable in sea water. In silt waters where pH is decreased down to 6.5 and less (Fairbridge 1971), intensive kaolinite formation is possible. While in the case of albite, anortite and chlorite the formation of authigeneous kaolinite is determined only by the decrease in pH, additional energy is required in the case of microcline, illites and montmorillonites. This energy was supplied during the life and decay of organic substances, as well as by spontaneous kaolinization of albite, anortite, chlorite, and micas. According to the calculations, the energy released during these processes is much greater than the energy required for kaolinization of feldspars, illites, and montmorillonites (Bobrov & Shchipakina 1990).

At the early stages of diagenesis in terrigenic (i.e. sand and sand-clay) sediments of sedimentation basins containing organic matter feldspars, micas, chlorite and other minerals were decomposed, certain elements were dissolved in colloid and true solutions under neutral and weak acid conditions (resulting from decreasing pH under the influence of organic matter), and authigeneous kaolinite and kaolinite concretions were formed. As a result of diffusion exchange between the silt and bottom waters and considerable deficit of silica in the sea water, silicic acid released during the reactions was removed. Intensification of these process owing to increasing acidity of the medium, bottom currents or increasing diffusion current with constant deficit of silica in the water, allowed the crystallization of alumina or mixed kaolinite-alumina concretions.

Since the physico-chemical conditions in the sediment varied, i.e. the generation of carbon dioxide and degassing of the sediment were slowed down, the silt waters pH gradually increased. In this case, the kaolinite or alumina core of the concretion adsorbed fine-dispersed illite matter, and polymineral zonal concretions were formed. The redox potential of the diagenetic process did not affect the formation of alumina and aluminosilicate concretions. In fact, the formation of concretion rocks was controlled by the contents of organic matter that favoured the increase in the contents of aluminosilicate or alumina colloids in the silts.

Diagenetic transformations resulted in redistribution and accumulation of not only rock-forming components but also numerous microelements (Tab. 3, X-ray fluorescence). Carbonic-kyanitic concretions have greater contents of V, Cu, Mo, Ga, Ge, rare-earth elements etc., as compared with the enclosing schists. As the concretions in question are of the non-sulfide type, it is evident that Cr, V, Ni, Co, Cu, Zn, Pb, Mo and Ge are associated with organic matter and are selectively accumulated during diagenesis. In zonal concretions, in spite of the metamorphism and the subsequent metamorphism, the information on the earlier diagenetic processes is preserved. This information is contained in zonal carbonic-muscovite-kyanitic concretions. Deficit of Eu and increasing contents of heavy rare-earth elements are observed in their central zones.

Authigeneous kaolinitic and illite-kaolinitic concretions and especially zonal formations in combination with the organic matter, concentrated microelements, which distinguishes authigeneous kaolinite from terrigeneous kaolinite. The latter is known to contain only a minor amount of microelements most of which are removed during the formation of kaolinitic residual rocks of the weathering crust.

Discussion and conclusion

The above mineralogical and geochemical peculiarities of the carbonic-kyanitic concretion rocks cannot be explained in terms of redeposition of highly chemically differentiated kaolinite residual rocks or laterite residual rocks of the weathering crust. First of all, continental formations, such as kaolin and bauxite clays, and bauxite have definite lithological zonality in the section. In the system of continental slope - coastal plain (lakes and marsh) - coastal-marine and marine zone (lagoons and the sea) they are arranged in the following sequence: multicolour continental deposits (bauxites, kaolin clays, sands) - carbonic and clay deposits (illite-kaolinitic clays, brown coals and sands) - coastal-marine and marine deposits (illite and montmorillonite clays, and sands). This is the most typical section of humid sedimentation in Phanerozoic (Ronov 1980) where kaolin and bauxite - leading residual rocks of the weathering crust serve as the source of the sediment.

The lithological zonality reconstructed for the Early Proterozoic section under study is as follows: quartz-feldspar rough detrital rocks and sands - sandstone chlorite-montmorillonite-illite and illitic clays - authigeneous kaolinitic and illite-kaolinitic concretions containing organic matter in the clay - sandstone sediment - illitic and sandstone clays. Comparison of these sections shows that they differ substantially, both in composition of the rocks and in their position in the section. In the region under study, Early Proterozoic pararocks were accumulated in intracraton shallow basins, where, at a certain stage in their existence, intensive development of organic life took place. Owing to the action of organic matter and the diagenetic processes, the chemically low-differentiated material of the residual rocks of the weathering crust was transformed into authigenic kaolinite and, probably free alumina, with subsequent formation of kaolinitic, alumina, zonal illite-kaolinitic concretions within the quartz-feldspar-micaceous material. The irregular distribution of the organic matter may have resulted in the formation of numerous concretion crystallization centres. Subsequent metamorphism turned these sedimentary formations into carbonic-kyanitic, muscovite-kyanitic, and andalusite-kyanitic metaconcretion high-alumina rocks. The presence of such concretions implies the significant role of diagenetic processes and the possible authigenic kaolinite formation in Pre-Cambrian sedimentation basins.

The indication of diagenesis found in highly metamorphosed Precambrian complexes allows more reliable reconstruction of the sedimentation conditions and correlation of the mineral composition of the matter redeposited from the continent for this period in the Earth' s history.

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